19p

X63 15175
N65-88742
Code 2d

Code 2d

SIXTY-EIGHTH QUARTERLY
REPORT

NASA CR-51003

The Institute for the Study of Metals

THE UNIVERSITY OF CHICAGO

~~"Available to NASA Offices" and NASA Centers Only.~~

FOR PRIVATE CIRCULATION ONLY

MARCH 1963

"Available to U.S. Government Agencies and U. S. Government Contractors Only."

SIXTY-EIGHTH QUARTERLY
REPORT

The Institute for the Study of Metals

THE UNIVERSITY OF CHICAGO

"Available to U.S. Government Agencies and U. S. Government Contractors Only."

FOR PRIVATE CIRCULATION ONLY

MARCH 1963

Available to NASA Offices and NASA Centers Only.

This report is a private communication of the Institute for the Study of Metals and must not be reproduced in whole or in part without special permission.

All articles contained herein have been submitted for publication in some professional journal, as indicated under the title of each article. It is urgently requested that no public reference to these articles be made until after their publication and that reference then be made to the appropriate periodical.

* * *

Acknowledgment is made to the following organizations for their sponsorship of the Institute for the Study of Metals:

Aluminium Laboratories, Ltd.
Borg-Warner Corporation
E. I. DuPont de Nemours and Company
Ford Motor Company
General Motors Corporation
Inland Steel Company
International Harvester Company
Socony Mobil Oil Company, Inc.
Standard Oil Company (Indiana)
Union Carbide Corporation
United States Steel Corporation

Acknowledgment is made to the Advanced Research Projects Agency, through Contract SD-89, and to the U. S. Atomic Energy Commission, through Contract No. AT(11-1)-357, for their support of the Institute for the Study of Metals.

Acknowledgment is also made to the following:

The U. S. Office of Naval Research for sponsorship of a program of studies (with Contract numbers) on:
antiferromagnetism [Nonr-2121(13)],
structure and properties of metallic solutions [Nonr-2121(11)],
the electron theory of solids [Nonr-2121(22)], and
the physics of fluids [Nonr-2121(20)];

The National Science Foundation for support of research (with Grant numbers given) on the following:
low temperature [NSF-GP-428],
the electron theory of solids [NSF-GP-510],
configurational and thermodynamic properties of polyelectrolytes and polar polymers [NSF-G-14968],
paramagnetic crystals [NSF-G-16824],
the electronic band structure of metals [NSF-G-20293],
thermodynamic properties of fused salt systems [NSF-G-19513],

field emission studies of adsorption and related phenomena [NSF-G-19618],
the physics of fluids [NSF-G-23068],
studies in theoretical chemistry [NSF-GP-426],
electron spectroscopy [NSF-GP-427], and
optical properties of metals [NSF-GP-490];

The Office of Ordnance Research, U. S. Army, for support of research on diffraction studies [DA-ARO(D)-31-124-G152], and on thin films of normal and superconducting metals [DA-ARO(D)-31-124-G442];

The Air Research and Development Command for support (with Contract numbers) of:
a study of the experimental investigation of the electronic properties of solids [AF-AFOSR-148-63],
studies in theoretical chemistry [AF-AFOSR-61-52] and [AF-AFOSR-369-63],
studies on the properties of solutions of metals dissolved in molten salts [AF-49(638)-1076], and
diffusion in solids and liquids at high pressures [AF-AFOSR-62-231];

The National Aeronautics and Space Administration for support of theoretical and experimental investigations of superconductivity [NASA-NsG-352];

The Alfred P. Sloan Foundation for support of research in physics and chemistry;

The U. S. Public Health Service for support of theoretical and experimental studies on electronic states of structureless media [Grant No. RG-9809]; and

The American Chemical Society, Petroleum Research Fund, for the study of transport properties in condensed systems.

CONTENTS

		Page
I	Experimental and Theoretical Study of Magnetic Breakdown in Magnesium M. G. Priestley, L. M. Falicov and Gideon Weisz	1
II	A Chain Model for Polyelectrolytes. IX. The Effects of Chain Length and Charge on the Friction Constant . . . . . George Thomson, Stuart A. Rice and Mitsura Nagasawa	2
III	Stages in the Education of a Physicist: An Attempted Solution of a Pedagogical Problem . . . D. H. Douglass, Jr. and M. W. P. Strandberg	3
IV	Low Temperature Calorimetry with Isothermal Shield and Evaluated Heat Leak . . . . J. W. Stout	4
V	Heat Capacities from 11 to 305°K, Entropies and Free Energies of Formation of L-Asparagine Monohydrate, L-Aspartic Acid, L-Glutamic Acid, and L-Glutamine . . . . . John O. Hutchens, Arthur G. Cole, R. A. Robie and J. W. Stout	5
VI	A Speculation Concerning the Nature of Bonding in Xenon Fluorine Compounds . . . Joshua Jortner, Stuart A. Rice and E. Guy Wilson	6
VII	A Far-Ultraviolet Spectroscopic Study of Xenon Difluoride . . . . . E. Guy Wilson, Joshua Jortner and Stuart A. Rice	7
VIII	A Spectroscopic Study of Xenon Tetrafluoride . . . . . Joshua Jortner, E. Guy Wilson and Stuart A. Rice	8
IX	The Heats of Sublimation of XeF_2 and XeF_4 and a Conjecture on Bonding in the Solids . . . . . Joshua Jortner, E. Guy Wilson and Stuart A. Rice	9

X Germanium as a Neutron Monochromator
. . . . C. S. Barrett, M. H. Mueller and L. Heaton 10

XI Heats of Mixing in Liquid Mixtures of Sodium-Potassium Iodide . . L. S. Hersh and O. J. Kleppa 11

XII Experimental Confirmation of the Landau Law in Couette Flow . . . . . R. J. Donnelly 12

XIII Statistical Mechanics of Defect Containing Solids. II. Ionic Crystals
. . . . . A. R. Allnatt and Morrel H. Cohen 13

I

EXPERIMENTAL AND THEORETICAL STUDY OF MAGNETIC BREAKDOWN IN MAGNESIUM*

M. G. Priestley,† L. M. Falicov and Gideon Weisz‡

(Accepted by The Physical Review)

Abstract

It is found that the energy band structure of magnesium in the symmetry plane ΓKHA of the Brillouin zone is such that regions of intersecting or nearly intersecting energy surfaces give rise to magnetic breakdown. A theoretical investigation of the profiles of the energy surfaces is carried out by means of an interpolation scheme based on values of the energy at the symmetry points taken from an existing orthogonalized-plane-wave (OPW) calculation. The energy gaps due to spin-orbit effects are computed using a three OPW approximation.

Experimental measurements of the de Haas-van Alphen effect for magnetic fields close to the c-axis are reported. A giant orbit of area larger than the cross section of the Brillouin zone is found. The experimental parameters for this orbit are in excellent agreement with the theoretical estimates.

*Supported in part by the Office of Naval Research, the National Science Foundation and the Atomic Energy Commission.

†The experimental work was done at the Royal Society Mond Laboratory, Cambridge, England.

‡ARPA Research Assistant.

II

A CHAIN MODEL FOR POLYELECTROLYTES. IX. THE EFFECTS OF CHAIN LENGTH AND CHARGE ON THE FRICTION CONSTANT*

George Thomson,† Stuart A. Rice and Mitsura Nagasawa‡
(Submitted to the Journal of the American Chemical Society)

Abstract

In this paper we report measures of self-diffusion and viscosity as a function of chain length and charge for some protonated and unprotonated amines, and for some disulfonate ions. It is found that:

a) The Peterlin theory of diffusion of short chain molecules is an accurate description of real systems.

b) The Peterlin theory of viscosity is qualitatively correct but quantitatively in error by a factor of two.

c) The placement of two charges on an ethylene imine leads to an extended molecule configuration.

d) The possibility of hydrogen bonding between uncharged ethylene imines and the water leads to zero slip between molecule and solvent. Therefore, classical hydrodynamic conditions are satisfied and the system behaves differently (larger friction constant) than would be expected from other studies in nonhydrogen bonding solvents.

e) When charges are placed on the ion the local water structure is modified, decreasing the efficacy (or even possibility) of hydrogen bonding. There is a range of variables wherein the friction constant per bead drops on going from the neutral molecule to the bolion because of the change in solvent interactions.

f) The transition from simple ion to polyion requires more than five charges per ion and longer chain lengths than considered herein.

---

*Work supported by the U. S. Public Health Service and the U. S. Atomic Energy Commission.

†NRC-NBS Postdoctoral Research Associate, National Bureau of Standards, Washington, D. C.

‡Permanent address: Department of Synthetic Chemistry, University of Nagoya, Nagoya, Japan.

III

STAGES IN THE EDUCATION OF A PHYSICIST: AN ATTEMPTED SOLUTION OF A PEDAGOGICAL PROBLEM*

D. H. Douglass, Jr.† and M. W. P. Strandberg
Department of Physics and Research Laboratory of Electronics
Massachusetts Institute of Technology
Cambridge, Massachusetts

(Submitted to the American Journal of Physics)

Abstract

In this paper, the stages in the development of a professional physicist are considered. One of the weak points of this process, the transition from student training to research training, is considered in some detail. A teaching experiment that has been performed at M.I.T. and was designed to bridge this gap is discussed. The results of this experiment lead us to propose this procedure as a partial solution to this particular problem.

*This work was supported in part by the U. S. Army Signal Corps, the Air Force Office of Scientific Research, and the Office of Naval Research.

†Dr. Douglass joined the faculty of the Institute for the Study of Metals and the Department of Physics of the University of Chicago on July 1, 1962. This paper represents work he has now prepared for publication but which was not actually done at the Institute.

IV

LOW TEMPERATURE CALORIMETRY WITH ISOTHERMAL SHIELD AND EVALUATED HEAT LEAK*

J. W. Stout

(To be published in Experimental Thermodynamics, Volume I, Calorimetry of Non-reacting Systems, John P. McCullough, editor, sponsored by IUPAC Commission on Thermodynamics and Thermodynamics and Thermochemistry.)

Abstract

Apparatus, techniques and methods of calculation for precise heat capacity measurements in the temperature range from 10 to 300°K are described in detail.

*This work was supported in part by the Office of Naval Research and the National Science Foundation.

V

HEAT CAPACITIES FROM 11 TO 305°K, ENTROPIES AND FREE ENERGIES OF FORMATION OF L-ASPARAGINE MONOHYDRATE, L-ASPARTIC ACID, L-GLUTAMIC ACID, AND L-GLUTAMINE*

John O. Hutchens, Arthur G. Cole, R. A. Robie
and J. W. Stout
(Accepted by the Journal of Biological Chemistry)

Abstract

Heat capacities from 11 to 305°K are reported for L-asparagine · H_2O(I), L-aspartic acid (II), L-glutamic acid (III) and L-glutamine (IV). Values of C_P°, S°, $(H^\circ - H_O^\circ)/T$ and $-(F^\circ - F_O^\circ)/T$ are tabulated as functions of temperature from 10 to 305°K. The available data concerning heats of combustion of these compounds are reviewed and, from selected values, enthalpies and free energies of formation are calculated. Values of $S^\circ_{298.15}$ in cal mole^{-1} deg^{-1} are (I) 50.10, (II) 40.66, (III) 44.98, (IV) 46.62. Values of $\Delta Hf^\circ_{298.15}$ in kcal mole^{-1} are (I) -259.70, (II) -232.64, (III) -241.32, (IV) -197.52, and of $\Delta Ff^\circ_{298.15}$ in kcal mole^{-1} are (I) -183.62, (II) -174.53, (III) -174.78, (IV) -127.30.

*The heat capacity studies reported here were supported by the U. S. Atomic Energy Commission, the National Institutes of Health and by the Wallace A. and Clara M. Abbott Memorial Fund of the University of Chicago. Support of the cryogenic facilities by the National Science Foundation is gratefully acknowledged.

VI

A SPECULATION CONCERNING THE NATURE OF BONDING IN XENON FLUORINE COMPOUNDS*

Joshua Jortner, Stuart A. Rice and
E. Guy Wilson
(Submitted to the Journal of
Chemical Physics)

Abstract

A bonding scheme in terms of molecular-orbital theory is presented for the recently discovered xenon fluorides. The predictions of the model are consistent with the available experimental data.

*Supported by the AFOSR (Grant 61-52), the USPHS, a nonspecific grant from the AEC to the Institute for the Study of Metals, and an ARPA grant for research on the science of materials at the University of Chicago.

VII

A FAR-ULTRAVIOLET SPECTROSCOPIC STUDY OF XENON DIFLUORIDE*

E. Guy Wilson, Joshua Jortner and
Stuart A. Rice
(Submitted to the Journal of the
American Chemical Society)

Abstract

The absorption spectrum of XeF_2 in the gas phase was studied in the vacuum-ultraviolet region to 1100 Å. Transition energies and oscillator strengths calculated by a molecular orbital treatment were found to be in good agreement with the experimental results.

*Supported by the AFOSR (Grant 61-52), the USPHS, a nonspecific grant from the AEC to the Institute for the Study of Metals, and an ARPA grant for research on the science of materials at the University of Chicago.

VIII

A SPECTROSCOPIC STUDY OF XENON TETRAFLUORIDE*

Joshua Jortner, E. Guy Wilson and
Stuart A. Rice
(Submitted to the Journal of the
American Chemical Society)

Abstract

The results of a spectroscopic investigation of XeF_4 in the ultraviolet region to 1100 Å are presented. Transition energies are found to be in good agreement with theory. The implications of a Jahn-Teller configurational distortion in the excited state are briefly considered.

*Supported by the AFOSR (Grant 61-52), the USPHS, a nonspecific grant from the AEC to the Institute for the Study of Metals, and an ARPA grant for research on the science of materials at the University of Chicago.

IX

THE HEATS OF SUBLIMATION OF XeF_2 AND XeF_4 AND A CONJECTURE ON BONDING IN THE SOLIDS*

Joshua Jortner, E. Guy Wilson and
Stuart A. Rice
(Submitted to the Journal of the
American Chemical Society)

Abstract

The heats of sublimation of crystalline solid XeF_2 and XeF_4 were determined to be 12.3 ± 0.2 kcal/mole and 15.3 ± 0.2 kcal/mole respectively. The dominant contribution to the stability of the solids arises from electrostatic interactions. A binding scheme for the intramolecular interactions in these molecules yields an adequate description of the intermolecular interactions in the solids.

*Supported by the AFOSR (Grant 61-52), the USPHS, a nonspecific grant from the AEC to the Institute for the Study of Metals, and an ARPA grant for research on the science of materials at the University of Chicago.

X

GERMANIUM AS A NEUTRON MONOCHROMATOR*

C. S. Barrett, M. H. Mueller† and L. Heaton†

(Submitted to Review of Scientific Instruments)

Abstract

A series of experiments was carried out using Ge crystals as neutron monochromators. The results indicated a considerable variation in monochromator efficiency as a function of the method used to introduce imperfections into the highly perfect crystals.‡ The use of deformation by compression was found to be the best. A 2.5 per cent reduction in thickness at 650° C of a crystal block 0.44 in. thick resulted in about a 30-fold increase in efficiency over the first crystal tested in its initial state. The dislocation density was increased from 5×10^3 to about 1.5×10^7 by this treatment.

*Work supported at the Argonne National Laboratory by the Atomic Energy Commission, and at the Institute for the Study of Metals in part by Office of Naval Research through Contract Nonr 2121(11).

†Argonne National Laboratory.

‡The crystals were furnished by Prof. H. Fritzsche; assistance in collecting data was furnished by R. Hitterman and H. Nott.

XI

HEATS OF MIXING IN LIQUID MIXTURES OF SODIUM-POTASSIUM IODIDE*

L. S. Hersh† and O. J. Kleppa
(To appear in Transactions of the Faraday Society)

Abstract

The enthalpies of mixing of liquid mixtures of sodium-potassium iodide have been measured calorimetrically at 700 ± 1°C, and obey the following expression:

$$-\Delta H^M / X_{NaI} X_{KI} = 507 + 47\, X_{NaI} \text{ cal/mole.}$$

Here ΔH^M is the molar enthalpy of mixing, while X_{NaI} and X_{KI} are the mole fractions of the two components. The results are compared with the corresponding expression for the binary nitrates. This permits a crude estimate to be made of the contribution of anion polarization to the enthalpy of mixing.

*This work has been supported by the National Science Foundation under Grant G-19513 to the University of Chicago. One of the authors (L. S. H.) wishes to acknowledge financial support from the U. S. Rubber Company.

†U. S. Rubber Company Predoctoral Fellow, 1961-62.

XII

EXPERIMENTAL CONFIRMATION OF THE LANDAU LAW IN COUETTE FLOW*

R. J. Donnelly
(To appear in Physical Review Letters)

Abstract

Using the ion technique developed in this laboratory it has been possible to verify directly that the equilibrium amplitude of a perturbation on the laminar flow grows as the square root of the difference between the Taylor number and the critical Taylor number. This result was predicted by L. Landau on very general grounds.†

*This research has been supported by a grant from the National Science Foundation for the Physics of Fluids and by a contract with the Office of Naval Research, NONR 2121(20), and by general grants from the U. S. Atomic Energy Commission and Advanced Research Projects Agency. During the period of this research the author has held an Alfred P. Sloan Research Fellowship.

†Landau and Lifshitz, Fluid Mechanics (Pergamon Press, New York, 1959), p. 103.

XIII

STATISTICAL MECHANICS OF DEFECT CONTAINING SOLIDS. II. IONIC CRYSTALS[*†]

A. R. Allnatt[‡] and Morrel H. Cohen
(Submitted to the Journal of Chemical Physics)

Abstract

The cluster expansions for the partition function and defect distribution functions derived previously are studied in detail for the case of ionic crystals with the object of calculating activity coefficients, defect concentrations, and defect distribution functions at low defect concentrations. A diagram classification procedure analogous to that in the Mayer theory of ionic solutions is used to obtain nondivergent expansions for defect activity coefficients and distribution functions. The discreteness of the lattice requires some modification of the diagram summation techniques employed in the solution theory. The theory of association of defects of the sort considered by Lidiard and Teltow is formulated more precisely in terms of the defect distribution functions. The formal multicomponent expressions are studied in more detail for the case of Schottky defects and impurity ions in a sodium chloride lattice. The results parallel those of the Mayer ionic solution theory, the principal difference being that the Debye-Hückel potential of average force appearing in the final Mayer expressions is everywhere replaced by $Ae^2 \exp(-\kappa R\xi)/RD$, where A and ξ are structure and concentration dependent and go to unity in the continuum limit.

As an example for the case of activity coefficients, calculations of the contributions from cycle diagrams and terms of next lowest order in concentration have been made for divalent impurity ions and cation vacancies in sodium chloride. The pair correlation function for oppositely charged defects and the degree of association have

[*]Supported in part by the Office of Naval Research and the National Science Foundation.

[†]Presented in part at the Eighteenth International Congress of Pure and Applied Chemistry, Montreal, August 1961.

[‡]N.A.T.O. Fellow, 1959-61. Present address: Department of Chemistry, University of Manchester, Manchester 13, England.

been calculated for the doped crystal. The theory reduces to that of Lidiard in the limit of zero concentration but differs at finite concentrations. However, calculation of the contribution of "triangle diagrams" to the activity coefficients indicates that below 500°C the expansions do not converge rapidly enough to be of value at concentrations of experimental interest because of the low dielectric constant. It was found that in the range of temperature and composition for which the theory converged, the parameters A and ξ differed little from unity.